NMR Study on the Electrochemically Generated Triphenylmethyl Anion

Mitsutoshi Okano,* Tsuyoshi Kugita,† Daijiro Ohtani, and Hiroshi Hamano

Department of Photo-Optical Engineering, Tokyo Institute of Polytechnics, Iiyama, Atsugi, Kanagawa 243-02

†Department of Material Science, The Nishi-Tokyo University, Uenohara-machi, Kitatsuru-gun, Yamanashi 409-01

(Received August 26, 1994)

The ^{13}C and ^{1}H NMR spectra of the triphenylmethyl anion, which had been generated by an electrochemical reduction of triphenylmethane in dimethylformamide at −40 °C, were successfully obtained. An anion having a tetrabutylammonium counter cation had ^{13}C chemical shifts similar to those for an anion with a lithium counter cation. An examination of the ^{1}H NMR spectra revealed that the reaction is a one-electron reaction. Experiments conducted under temperature control showed that the anion is fairly stable below −20 °C. Decomposition of the anion above −20 °C was suggested to be hydrogen abstraction from the β-position of a tetrabutylammonium cation by a triphenylmethyl anion (Hofmann decomposition of the ammonium cation).

Spectroscopic investigations of electro-generated active species, besides in-situ UV-vis spectroscopy[1] and ESR,[2] have been very much limited because the electrochemical set-up often limits the analytical methods which can be used in situ, and electro-generated active species are usually short-lived,[3] which makes ex-situ measurements extremely difficult. For such reasons, NMR, one of the most commonly used and most powerful tools in organic chemistry, has not been utilized to study electro-generated species, even though in order to clarify the characteristics of electro-generated organic species in an electrolyte solution, information from NMR measurements is essential. This is the reason the authors have been looking for a system with which electro-generated active species can somehow be accumulated which are worth investigating using NMR.

In 1990, Fuchigami et al. reported that triphenylmethyl anion can be accumulated at low temperature according to the following electrochemical reaction:[4]

$$Ph_3CH \xrightarrow{e-1/2H_2} Ph_3C^- \qquad (1)$$

The authors have noticed that the reaction product, $[Bu_4N]^+Ph_3C^-$, was worth studying with NMR because anions with ammonium cations had been scarcely studied in common organic chemistry, while such anions are often encountered and are very important in electroorganic chemistry.[5] The authors also applied their method to the other 14 group element-centered compounds and revealed that Eq. 2 is a novel reaction in which the characteristics of all 14 group element-centered compounds can be discussed systematically:[6,7]

$$R^1R^2R^3EH \xrightarrow{e-1/2H_2} R^1R^2R^3E^- \qquad (2)$$
$$E = C, Si, Ge, Sn, Pb$$

Here, an NMR study of the electro-generated triphenylmethyl anion is reported. ^{13}C NMR gives very precise information concerning the electronic state of the anion, and ^{1}H NMR gives quantitative information about the anion. This qualitative and quantitative information is often very important for understanding electroorganic reactions, and, off course, is not accessible with the conventional electrochemical analyses themselves and the other experimental methods other than NMR. The purpose of this paper is to show, for electroorganic chemistry, how important the information obtained with NMR is when measurements are allowed.

Experimental

Materials. Triphenylmethane (Ph_3CH) was recrystallized from ethanol and dried under vacuum. Tetrabutylammonium tetrafluoroborate (TBATFB) was reprecipitated from ethyl acetate/pentane and dried under vacuum. Dimethylformamide (DMF) was dried with calcium hydride, distilled under a nitrogen atmosphere, and stocked in the presence of molecular sieves.

Electrolysis. Platinum wires were used as the anode and the cathode. A two-compartment cell was employed in order to accumulate the anion species in the cathode compartment. Typical electrolysis conditions were as follows. The electrolyte solution contained 0.1 M Ph_3CH and 0.3 M TBATFB (1 M=1 mol dm^{-3}). The solution was degassed

under vacuum immediately before use and transferred into a cell previously flushed with argon. The cell was immersed in a cold ethanol bath at −40 °C. After waiting for the electrolyte solution to cool down, the electrolysis was started with a constant current of 10 mA controlled by a potentio/galvano stat. The electrolysis was stopped when the electricity, monitored by a coulometer, reached a previously calculated value.

Measurement of NMR Spectra. The anion accumulated in the catholyte solution. After electrolysis, an alliquot of the solution was carefully transferred into a cold NMR tube under an argon atmosphere by the use of a pipette with a cold ethanol jacket at −40 °C. In order to obtain an NMR lock signal, a cold inner tube containing deuterated acetonitrile was inserted into the above NMR tube. The NMR tube was sealed with a piece of paraffin film and kept below −40 °C prior to a measurement. Under temperature control, NMR measurements were performed as soon as possible, normally being started within 15 min from the sampling. A 500 MHz NMR spectrometer (JEOL, alpha 500) was used for the measurements. DMF ($\delta=36.09$ for ^{13}C NMR and $\delta=8.01$ for ^1H NMR) was used as a reference at all temperatures. NMR measurements had no problem when the concentration of the electro-generated active species was between 0.1 and 0.001 mol dm^{-3} in the electrolyte solution. The authors believe that NMR has an ability to measure samples of much lower concentration.

Reaction with Organic Halides. After accumulation of the anion in the catholyte, 50 μl of a pre-cooled (typically below the temperature of the catholyte, −40 °C when possible) halide was added to each electrolyte from the injection ports of the electrolysis cell. The mixture was stirred for 30 min. The solvent was evaporated and the reaction product was taken up in ether. The yields were determined by gas chromatography using decane as the internal standard.

Measurement of the Thermal Decomposition Rate. Cyclohexane (ca. 3.7×10^{-5} mol) was added to the electrolyte solution before electrolysis, and was used as the internal standard. The integrated area for the meta proton of triphenylmethyl anion was compared with that of cyclohexane on a ^1H NMR spectrum. Measurement of the ^1H NMR spectrum took less than 5 min, and was performed every 30 min. At between 0 and −15 °C, the decomposition reaction had a rate suitable for the above-mentioned measurement sequence.

Measurement of UV-vis Spectra. The anion solution was transferred to a UV cell for the cryostat (Oxford, DN1704) by means of a method similar to that employed in the measurement of the NMR spectra. The cell had an optical path of 1 cm. Electrolysis was stopped at an early stage of anion accumulation in order to obtain an anion solution having absorption suitable for a UV measurement.

Results and Discussion

Generation and Characterization of Triphenylmethyl Anion ($[Bu_4N]^+Ph_3C^-$). The anion species, which was easily recognized due to their characteristic red color, gradually accumulated in the catholyte as the electrolysis proceeded. As far as could be judged from the color, the anion species seemed to be stable at −40 °C.

^{13}C NMR spectra of the electrolyte solution before and after the electrolysis are shown in Fig. 1. Though the signals of the starting compound (Ph_3CH) were still present in the spectrum (b), five new peaks were observed at 149.5, 128.5, 123.8, 113.6, and 90.2 ppm, respectively. Table 1 summarizes the ^{13}C chemical shifts. The observed new peaks were easily assigned, as shown, because the shift values were almost the same as those reported in the literature for anions with metal counter cations.[9] These observations agree with those of K. Takahashi, in that the effects of the cations and solvents were weak on the triphenylmethyl anion.[9] Therefore, the electrochemical formation of $[Bu_4N]^+Ph_3C^-$ was proved by NMR. Signals from $[Bu_4N]^+$ did not show any change from the supporting electrolyte, suggesting that $[Bu_4N]^+Ph_3C^-$ is not a contact ion pair, but is a separated ion pair. This fact is not surprising, because usual anions, such as fluorenyllithium, are known to be a separated ion pair, even in tetrahydrofuran, which is a less-polar solvent compared with DMF.[10]

Fuchigami et al. have reported that $[Bu_4N]^+Ph_3C^-$ behaves as a peculiar base.[4] In order to determine the reason for this observation, a precise comparison of the obtained shift values with those of the reported values for the anions with Li as the counter cations was made. Before such a comparison the temperature effect on the NMR shift values had to be clarified, since the values for the anions were obtained at −40 °C. For this reason, the NMR spectra of Ph_3CH were taken at room temper-

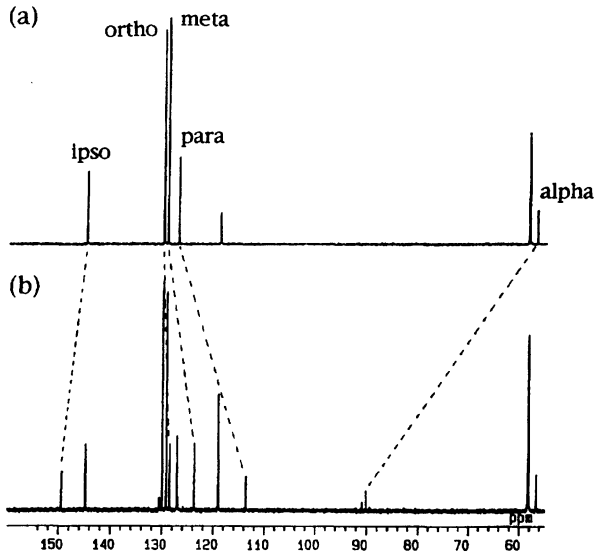

Fig. 1. ^{13}C NMR spectra of the electrolyte solution; (a) before the electrolysis (containing Ph_3CH) at room temperature and (b) after the electrolysis (containing Ph_3CH and $[Bu_4N]^+Ph_3C^-$), measured at −40 °C. The signals at 119 and 58 ppm are that of deuterated acetonitrile in the inner NMR tube and that of tetrabutylammonium tetrafluoroborate, respectively.

Table 1. ^{13}C NMR Chemical Shifts of Triphenylmethyl Anions and Triphenylmethane

	^{13}C NMR chemical shifts/ppm				
	ipso	ortho	meta	para	alpha
Ph_3CH at r.t.[a]	144.9	130.0	129.1	127.0	57.2
Ph_3CH at −40 °C[a]	144.8	130.0	129.1	127.0	56.7
Ph_3CH[b]	143.8	129.4	128.2	126.2	56.8
Ph_3CH[c]	145.2	129.5	130.7	127.5	58.2
$[Bu_4N]^+Ph_3C^-$ at −40 °C[a]	149.5	123.8	128.5	113.6	90.2
$Li^+Ph_3C^-$ [c]	150.5	124.4	128.3	113.3	91.0
$K^+Ph_3C^-$ [c]	148.9	123.9	128.9	114.4	88.2

a) This work. b) Ref. 8, temperature not reported. c) Ref. 9, temperature not reported.

ature and −40 °C, and the shift values were compared. Only the alpha carbon gave significantly different values between room temperature and −40 °C. The difference, however, was not large (0.5 ppm). We now compare the shift values for $[Bu_4N]^+Ph_3C^-$ at −40 °C and those for $Li^+Ph_3C^-$ and $K^+Ph_3C^-$. The shift values for $[Bu_4N]^+Ph_3C^-$ fell between those for $Li^+Ph_3C^-$ and $K^+Ph_3C^-$. This result tells us that the electronic state of $[Bu_4N]^+Ph_3C^-$ is very similar to those of $Li^+Ph_3C^-$ and $K^+Ph_3C^-$. In order to obtain more information concerning the electronic state of $[Bu_4N]^+Ph_3C^-$ in DMF, the absorption peak of $[Bu_4N]^+Ph_3C^-$ was also measured. The peak value (500 nm) coincided with the reported value, indicating the same electronic state with $Li^+Ph_3C^-$ in tetrahydrofuran.[11] It was thus concluded that $[Bu_4N]^+Ph_3C^-$ has mostly the same character as $Li^+Ph_3C^-$ and $K^+Ph_3C^-$. The authors believe that the peculiar reactions observed by Fuchigami et al. occurred because of the peculiarity in the solvent system, but not because of the anion character.

The ^1H NMR spectra are shown in Fig. 2. Table 2 summarizes the ^1H chemical shifts. Again, the observed peaks were easily assigned, as shown. The values were almost the same as those reported for the anions with metal counter cations.[12,13] The use of a 500 MHz NMR spectrometer allowed us to observe separate peaks for the ortho, meta, and para protons for Ph_3CH. (As far as the authors know, such shift values has not been reported. ^{13}C–^1H COSY was performed and all assignments were made. Our assignments of the ^{13}C chemical shifts agreed with those of Proulx and Smith.[8]) Thus, from the ^1H NMR spectrum, the content of the anion could be calculated based on the integrated values for the para proton of the anion and for the mother compound. A careful experiment performed with utmost

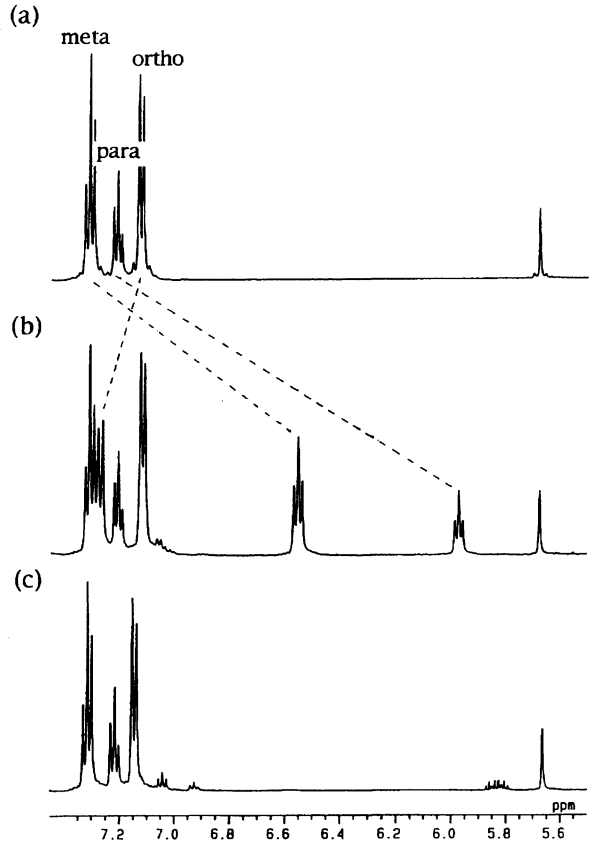

Fig. 2. ^1H NMR spectra of the electrolyte solution; (a) before electrolysis (containing Ph_3CH) at room temperature, (b) after the electrolysis (containing Ph_3CH and $[Bu_4N]^+Ph_3C^-$), measured at −40 °C, and (c) after the electrolysis (containing Ph_3CH), measured at 20 °C.

Table 2. ^1H NMR Chemical Shifts of Triphenylmethyl Anions and Triphenylmethane

	^1H NMR chemical shifts/ppm		
	ortho	meta	para
Ph_3CH at r.t.[a]	7.17	7.32	7.22
Ph_3CH at −40 °C[a]	7.13	7.31	7.21
$[Bu_4N]^+Ph_3C^-$ at −40 °C[a]	7.28	6.56	5.98
$Li^+Ph_3C^-$ [b]	7.25	6.46	5.90
$K^+Ph_3C^-$ [b]	7.23	6.58	6.02
$Li^+Ph_3C^-$ at 29 °C[c]	7.31	6.52	5.95

a) This work. b) Ref. 12, temperature not reported. c) Ref. 13.

attention, and such a calculation, revealed that 51% of $[Bu_4N]^+Ph_3C^-$ and 49% of Ph_3CH existed in the electrolyte solution after 1 F per mole of electrolysis. Also taking into account that some part of the electrogenerated anions decomposed before completion of the NMR measurement, mainly during the transfer procedure from the electrolysis cell to the NMR tube, it was clarified that the starting compound was mostly consumed after 1 F per mole of electrolysis. It was therefore concluded that the electrochemical reduction of Ph_3CH is a one-electron reduction of Ph_3CH (Eq. 3). The fate of H· is not known.

$$Ph_3CH \xrightarrow{e-1/2H_2} Ph_3C^- + H\cdot \quad (3)$$

In order to know the reactivity of the anion, reactions with methyl iodide and bromobenzene were carried out. The yields were 50 and 15%, respectively. Thus, the anion had sufficient reactivity at −40 °C. Since bromobenzene freezes at −31 °C, strictly identical reaction conditions have not been achieved. The reaction with bromobenzene, however, seemed to be slower, judging from the change in the color of the solution. Probably, a steric hindrance caused the observation. A reaction with oxygen was also performed. The introduction of oxygen gas caused a spontaneous disappearance of the color. The product may have been $[Bu_4N]^+Ph_3COO^-$.

Decomposition of the Anion. Figure 2(c) shows the spectrum after the temperature was increased (at 20 °C). The signals for $[Bu_4N]^+Ph_3C^-$ completely disappeared. The signals attributable to Ph_3CH grew with very small signals due to unknown by-products. At the same time, new signals appeared in addition to those of $[Bu_4N]^+$, suggesting the decomposition of $[Bu_4N]^+$. The decomposition product was probably tributylamine (Bu_3N), because the signals very closely resembled those of Bu_3N in DMF measured in a separate experiment.

In order to obtain more information concerning the decomposition reactions, Ph_3CH was reduced in the presence of tetraethylammonium tetrafluoroborate (TEATFB). The characteristic red color suggested the formation of $[Et_4N]^+Ph_3C^-$. The UV-vis spectrum proved its existence. However, even though the transferred solution retained its characteristic color, NMR signals from the anion were not obtained, probably because most of the anion species had been decomposed during the transfer procedure from the electrolysis cell to the NMR tube. It was still clear that $[Et_4N]^+Ph_3C^-$ was obtained, and that they had less thermal stability compared with that of $[Bu_4N]^+Ph_3C^-$.

These results suggested that counter cations concern the decomposition of the anion. The most probable decomposition mechanism is hydrogen abstraction at the β position of the ammonium ion by Ph_3C^- (Hofmann decomposition of the ammonium ion), as shown in Eqs. 4 and 5.

$$[Bu_4N]^+Ph_3C^- \rightarrow Ph_3CH + Bu_3N + CH_2{=}CHCH_2CH_3 \quad (4)$$

$$[Et_4N]^+Ph_3C^- \rightarrow Ph_3CH + Et_3N + CH_2{=}CH_2 \quad (5)$$

Hofmann's rule also tells us that Eq. 5 will occur more easily than Eq. 4.

Reaction Rate of the Decomposition. The rate equation for the reaction in Eq. 4 can be written as $k[Ph_3C^-][Bu_4N^+]$, or, since $[Bu_4N^+]$ is in excess, $k'[Ph_3C^-]$, where $k'=k[Bu_4N^+]$. In order to determine the decomposition rate, the concentration of $[Bu_4N]^+Ph_3C^-$ was measured as a function of time at various temperatures. A first-order analysis of the data gave fairly good straight lines. The thus-obtained k' values were 5.6×10^{-5} s^{-1} at −15 °C, 1.1×10^{-4} s^{-1} at −10°C, 2.4×10^{-4} s^{-1} at −5 °C, and 5.2×10^{-4} s^{-1} at 0 °C. Arrhenius plots gave an activation energy of 8.6×10^4 J mol^{-1}. A more precise study concerning the reaction dynamics was not possible, since our experimental conditions were greatly limited.

Conclusion

Generally speaking, when the experimental conditions are met, ^{13}C NMR (1) gives data concerning the electro-generated active species as they are in the electrolyte solution, and clearly proves their generation, (2) gives precise information about the electronic state of the electro-generated active species, and (3) gives abundant information about the effect of the experimental conditions which influence the electro-generated active species.

^1H NMR (4) gives the amount of electro-generated active species, which is usually guessed based on the electricity passed through the circuit or the amount of reaction product, and (5) enables kinetic studies when the reaction rates are suitable for the measurement sequence.

This work was supported by a Grant-in-Aid for Scientific Research on Priority Areas (No. 236) for M. O. (No. 05235247) from the Ministry of Education, Science and Culture.

References

1) H. Gerishcer, *Faraday Discuss. Chem. Soc.*, **56**, 7 (1973).

2) I. B. Goldberg and T. M. McKinney, "Principles and Techniques of Electrochemical-Electron Spin Resonance Experiments," in "Laboratory Techniques in Electroanalytical Chemistry," ed by P. T. Kissinger and W. R. Heineman, Marcel Dekker, New York (1992), p. 675.

3) W. J. Albery, *Trans. Faraday Soc.*, **62**, 1915 (1966).

4) T. Fuchigami, K. Suzuki, and T. Nonaka, *Electrochim. Acta*, **35**, 239 (1990).

5) S. Torii, "Yuki-denkai-gosei," Kodansha Scientific, Tokyo (1981), Chap. 1.

6) M. Okano, T. Kugita, and K. Mochida, *J. Electroanal. Chem.*, **356**, 303 (1993).

7) T. Kugita, M. Okano, T. Ohtsuka, and K. Mochida, *Denki Kagaku*, **62**, 1304 (1994).
8) T. W. Proulx and W. B. Smith, *J. Magn. Reson.*, **23**, 477 (1976).
9) K. Takahashi, Y. Kondo, and R. Asami, *Org. Magn. Reson.*, **6**, 580 (1974).
10) H. Reich and J. Borst, *J. Am. Chem. Soc.*, **113**, 1835 (1991).
11) R. Waack and M. A. Doran, *J. Am. Chem. Soc.*, **85**, 1651 (1963).
12) E. Buncel, T. Venkatachalam, B. Eliasson, and U. Edlund, *J. Am. Chem. Soc.*, **107**, 303 (1985).
13) R. Cox, E. Janzen, and W. Harrison, *J. Magn. Reson.*, **4**, 274 (1971).